PHOTOPHYSICAL PROPERTIES OF PYRENE, 2, 7 DIAZAPYRENE AND 1,3-BIS(β NAPHTHYL)PROPANE

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The luminescence properties of Van Der Waals' dimers and clusters of pyrene and diazapyrene have been investigated. Excimers, dimeric species which are associative in an excited electronic state and dissociative in their ground state, have long been established and play an important role in many areas of photochemistry. My work here focuses on the luminescence and absorption properties of ground state dimers/aggregates, which are less understood, and allows further characterization of the ground state and excited state association of these aromatic molecules.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1. Luminescence Theory

Luminescence is the emission of light from a molecule in an excited electronic state. When a molecule absorbs light of a given wavelength, λ_1, its electrons are excited to higher energy levels. These 'excited state' electrons subsequently decay to a lower energy state – their 'ground-state'. When an electron decays from an excited state to its ground-state, it may emit light of wavelength λ_2, which may be observed by the naked eye, or with a spectroflourometer.[1,2] Electronic decay accompanied by the emission of light is called radiative decay. When an electron decays to its ground-state without the emission of light, the transition is said to be non-radiative. Generally, the wavelength of emission, λ_2, is longer than the excitation wavelength, except in resonance emission when $\lambda_1=\lambda_2$.[1,2]

The radiative and nonradiative transitions that lead to the observation of molecular photoluminescence are typically illustrated by an energy level diagram called the Jablonski diagram.[2] A Jablonski diagram explains the mechanism of light emission in most organic and inorganic luminophores. On the diagram,

electrons in the ground-state are either assigned a singlet (S_1) state, while electrons in excited electronic states may be either singlet (S_1, S_2 , S_n) or triplet (T_1, T_2, T_n).[1,2]

A host of non-radiative and radiative processes usually occur following the absorption of the light, before and during the observation of luminescence. The following is a description of the different types of non-radiative and radiative processes.

1.1.1. Non-Radiative Processes

Vibrational relaxation: Upon excitation, electrons of a molecule within a given electronic state (S_n), may move to a higher vibrational energy level within the same electronic state. These electrons normally decay rapidly to the lowest vibrational level of the excited electronic state. This non-radiative process is called a “vibrational relaxation.” Vibrational relaxation occurs almost instantaneously within about 10^{-14}-10^{-2} s,[1] a time much shorter than typical luminescence lifetimes. Therefore, such processes occur prior to luminescence.

Internal Conversion: If electrons in a molecule are excited to an energy state higher than S_1, a rapid non-radiative decay usually occurs to the lowest-energy singlet excited state (S_1). Relaxation processes between electronic states of like spin multiplicity such as S_1 and S_2 are called ‘internal conversions’. These

processes normally occur on a time scale of 10^{-12} s. Internal conversions may occur for molecules in their triplet state as well.

Intersystem crossing: Non-radiative relaxation may also occur between states with different spin multiplicities. A process in which relaxation proceeds between excited states of different spin multiplicity is called 'intersystem crossing'.[1] The transition from S_1 to T_2 is an example of an intersystem crossing. Intersystem crossing is a rare event in electronic decay, because an electron moves from a singlet state to a triplet state and the spin multiplicity is not conserved. Because of the lower probability for intersystem crossing processes, they occur more slowly (~10^{-8} s) than internal conversions.

1.1.2. Radiative Processes

Flourescence vs. Phosphorescence: Luminescence bands can be either fluorescent or phosphorescent. Subsequent to excitation and prior to radiative emission, an electron undergoes vibrational relaxation and intersystem crossing, it may then follow one of two paths: 1) radiative decay from the lowest excited singlet state S_1, which is called fluorescence; or 2) it may undergo intersystem crossing and decay from a triplet (T_1) state to the singlet ground-state (S_0). In this case, the resulting emission is called phosphorescence.

The spin selection rule for electronic transitions (both absorption and emission) states that 'spin-allowed' transitions are those in which the spin

multiplicity is the same for the initial and final electronic states.[1] Therefore, spin-allowed transitions are more likely to take place than spin-forbidden transitions. In fluorescence, it is worth noting that the emission of light occurs from an excited electronic state that has the same spin multiplicity as the ground electronic state. Fluorescent emissions are therefore spin-allowed and occur very rapidly. The average lifetimes of the excited states responsible for fluorescence are typically $<10^{-6}$ s.[1]

Electronic transitions between states of different spin multiplicity are 'spin-forbidden', and as such, are less probable than spin-allowed transitions.[1] Intersystem crossing, as explained above facilitates the decay of electrons from a singlet state to a triplet state, and results in phosphorescence. Since transitions leading to phosphorescence are spin-forbidden, phosphorescent lifetimes are usually very long.

Generally, fluorescence lifetimes are on the order of sub-microseconds while phosphorescence lifetimes are on the order of microseconds or longer.

1.1.3. Delayed Fluorescence

Sometimes the observed lifetime for the fluorescence of a given luminophore may be longer than expected. This is called delayed fluorescence and occurs when an electron in a singlet excited state, undergoes intersystem

crossing, and then reverts back to the singlet state before undergoing fluorescent decay.[2]

CHAPTER 2

PHOTOLUMINESCENCE OF PYRENE

2.1. Excimer Formation

An excimer is simply an excited dimer. There are two forms of excimers discussed in current literature: dynamic excimers and static excimers.

2.1.1. Dynamic Excimers

A dynamic excimer, which is the most widely known form of excimers, was first discovered and defined by Birks[1] as one, which is formed when an excited monomer interacts with an identical ground-state monomer. This interaction is governed by equation 1:

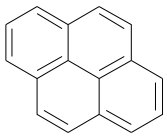
$$A^* + A \rightarrow {}^*[A\text{-}A] \qquad (1)$$

where A represents a ground-state monomer and A* a monomer in its excited state.

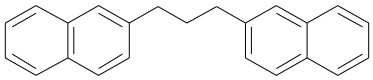
The classical features that identify excimer emissions in poly-nuclear aromatic hydrocarbons (PAHs) are their unstructured profile and monomer excitation route preceding the formation of the excited-state dimer.[1,3] Pyrene is the prototypical example of PAHs that exhibit excimer fluorescence upon increasing the concentration in solution or in solid state.

2.1.2. Static Excimers

Static excimer formation is a more recently discovered form of excimer. It occurs when pre-associated dimers are excited and subsequently, undergo excimer emission.



Pyrene



1,3-Bis(β-naphthyl)propane
(DNP)

Figure 2.1. Molecular structures of pyrene and DNP

A potential energy diagram for the approach and collision of an excited pyrene molecule (Py*) and a pyrene molecule in its ground-state (Py) would show that at a large separation distance, the emission spectrum produced is that of Py*. As the two molecules approach each other, their attractive force depresses the excited state potential energy curve. Eventually excimer formation causes a minimum to occur in the curve. Emission from the curve occurs according to the Franck-Condon principle, which states that due to negligible nuclear displacement on excitation, electrons undergo vertical transitions into higher electronic states. It is widely accepted[2,3] that if the separation of Py* and Py corresponds to a point on the repulsive part of the ground-state potential curve, Franck-Condon emission will lead exclusively to repulsive states on the ground surface. Upon colliding, Py* and Py will fly apart rapidly.[3] The lack of

vibrational structure, characteristic of excimers, is thereby attributed to the short lifetime and indefinite character of the *[Py–Py] state. These excimers are sometimes referred to as *dynamic excimers*. Recent literature,[3,4] however, disputes the theory that the ground-state is purely repulsive, and introduces the concept of *ground-state dimers* in pyrene. The excitation and subsequent emission of these dimers is said to lead to an associative state. The spectroscopic data - a broad emission profile - presented as evidence for the existence of associative dimer emissions is, however, incongruous with the widely accepted explanation for the broad, spectroscopic profile exhibited by excimers. The assertion that there is no difference between a shallow minimum in the potential of a ground-state dimer and a purely repulsive potential of the ground-state dimer,[4] may explain this data if a shallow minimum for the ground state is assumed. Recently, however, definitive data for the existence of ground-state dimer excitation and subsequent emission in the form of absorption spectra and structured excimer emission in pyrene solutions has been published.[4]

My experiments reproduce this unusual photophysical behavior contrary to the aforementioned classical features of pyrene excimers in solutions. These findings are further characterized by monitoring the temperature-dependent behavior of ground-state dimer emission (versus classical excimer emission), and calculating the vibronic spacing and the formation constant for the dimer emission and absorption respectively. These findings are expanded to include data on the ground-state dimer absorption and emission of pyrene single

crystals, (Figure 2.1). Finally, I explore the photophysical properties of 1,3-Bis(β-dinaphthyl)propane (DNP) in solid state and in concentrated solutions, for evidence of ground state dimer absorption and emission.

2.2. Experimental Section

Commercially available pyrene was purified by sublimation and crystal growth before the purified material was used. DNP was prepared according to Chandross and Dempster's procedure.[5] The crude DNP was sublimed in vacuum twice at 150 ^{o}C and then re-crystallized from hexane, m.p. 101-102 ^{o}C.

The luminescence measurements were carried out for crystalline materials. Steady-state luminescence spectra were acquired with a PTI QuantaMaster Model QM-4 scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The emission spectra were corrected for the detector wavelength-dependent response. The excitation spectra were also corrected above 250 nm due to the unreliability of the correction methods at short wavelengths below 245 nm, at which the samples here absorb and the xenon lamp output is rather low. Temperature-dependent studies were acquired with an Oxford optical cryostat using liquid nitrogen as the coolant. Lifetime data were acquired using a nitrogen laser interfaced with a tunable dye laser and a frequency doubler, as part of fluorescence and phosphorescence sub-system add-ons to the PTI instrument. The 337.1 nm line of the N_2 laser was used to pump a freshly-prepared 5×10^{-4} M solution of the organic continuum laser dye PBBO in toluene/ethanol (7/3).

Absorption spectra were acquired with a Perkin-Elmer Lambda 900 double beam UV/VIS/NIR spectrophotometer. Solutions of crystalline samples were prepared in HPLC grade cyclohexane and butyronitrile.

2.3. Results and Discussion

Figure 2.2a shows that in addition to the established monomer absorption peaks at 388nm and less, absorption peaks at 427nm and 451nm were also obtained for 0.1M pyrene solution. Similar long-wavelength absorption peaks were first reported by Khakel[4] who studied the photo-physics of pyrene aggregates in saturated solutions. He also reported the formation of a structured profile when saturated pyrene solutions were selectively excited at 390nm and 440nm. In Figure 2.2c, this structured emission profile is reproduced by exciting at 390nm and 400nm. I chose not to excite at wavelengths higher than 400nm because the range of the emission profile spans that region. The vibronic spacing calculated for the structured excimer emission of 0.1M pyrene solution is ~ 1360cm^{-1}, which corresponds to that calculated for the monomer. A value of 4533 M^{-1} was calculated for the formation constant,[6] and ΔG was found to be -20.8 KJ/mole for the ground-state pyrene dimer based on the quantitative data in Figure 2.2c. The electronic absorption peak at 427 nm has been monitored also at different temperatures and similar analytical approaches have been applied to obtain the free energy of activation, ΔG_{1n}. Linear fitting of ΔG_{12} vs. T (K) gives rise to ΔH of -66.98 kJ/mole and ΔS_{12} of 0.194 kJ/K-mole. The data for these

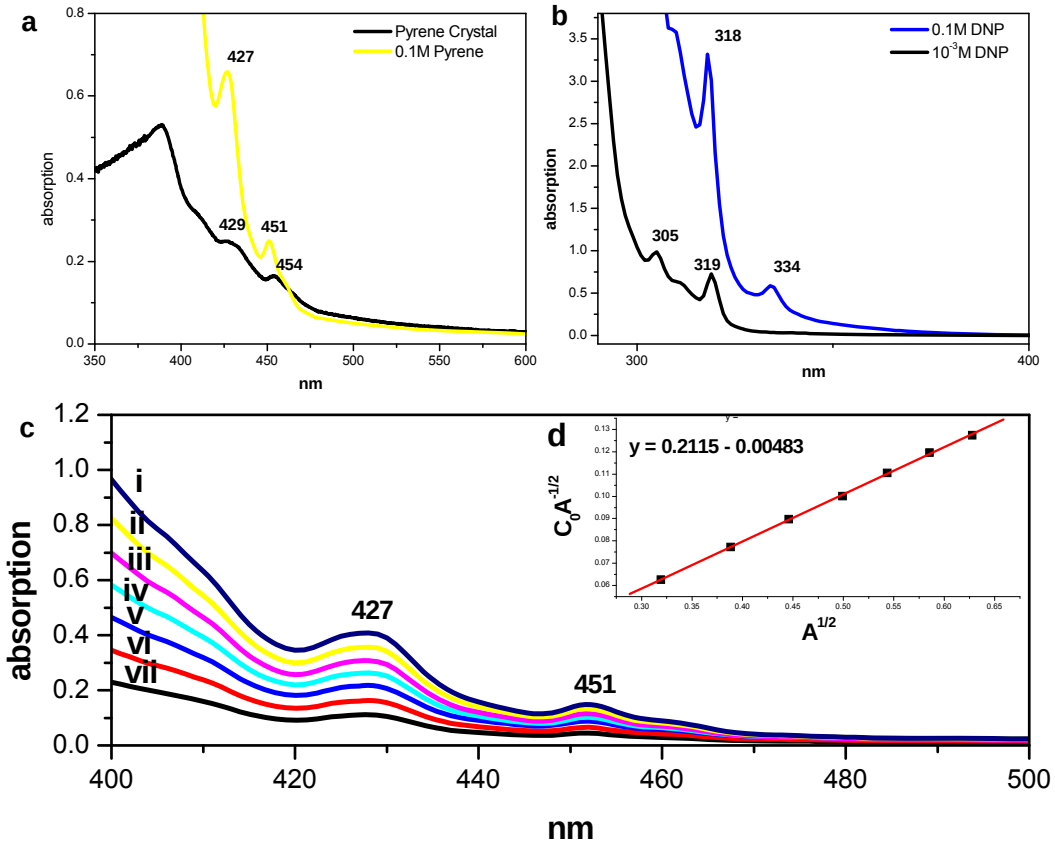


Figure 2.2 (a) Absorption spectra of 0.1M pyrene in cyclohexane (—), and pyrene crystal (—) (b) Absorption spectra of 0.1M (—), and 10^{-3}M (—) DNP in cyclohexane. (c) Absorption spectra of solutions of pyrene (i)0.08M, (ii)0.07M, (iii)0.06M (iv)0.05M, (v)0.04M, (vi)0.03M, (vii)0.02M. (d) A linear plot of $c_0A^{-1/2}$ vs. $A^{1/2}$ for the above concentrated solutions of pyrene. The absorbance values were taken for the absorption feature near 427nm. All spectra are at ambient temperature.

calculations are summed up in Figure 2.2. All the calculations in Figures 2.2d and 2.3 are based on the equation 2:[6]

$$C_oA^{-1/2} = (2/\{\varepsilon_2 b\})A^{(2-1)/2} + (K_{12}\varepsilon_2 b)^{-1/2} \qquad (2)$$

Where C_o is the initial pyrene concentration, A the maximum absorbance at 427nm and b is the light path (10cm).[6] A look at Figure 2.2d shows that plotting $C_oA^{-1\backslash 2}$ vs $A^{1\backslash 2}$ produces a near perfect fit. This further supports the assertion that the absorption peak at 427nm is due to dimerization in pyrene.

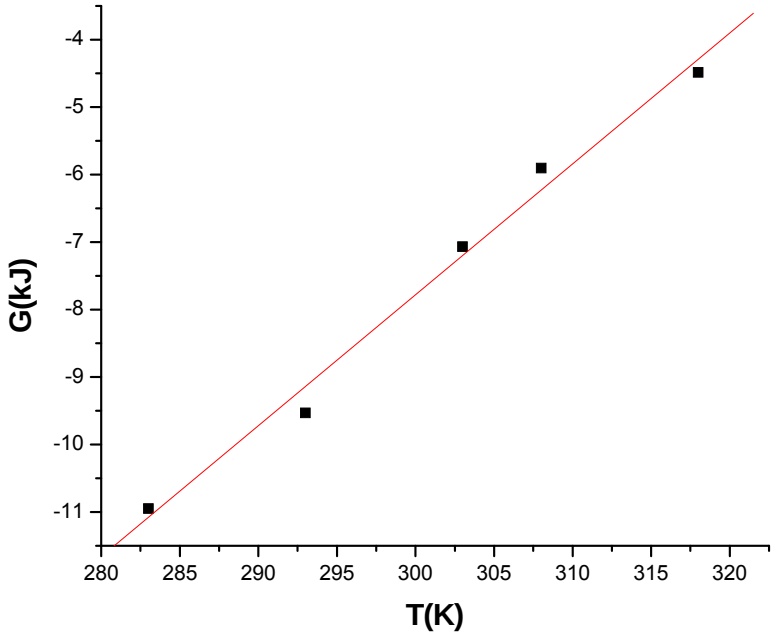


Figure 2.3. Plot of ΔG vs T(K) of pyrene dimers at 427 nm. Slope, ΔS = 0.194 kJ/K-mole, and Y-intercept ΔH = -66.98 kJ/mole.

In Figure 2.2a it is shown that similar long-wavelength absorption peaks are seen in pyrene crystals. These absorption bands in the visible region explain the yellow color of these crystals. This is something which literature on pyrene, till date, has failed to recognize. Since crystals of pyrene have been proven to exist

as dimeric molecular units with an inter-planar separation of 3.53 Å,[7,8] it is reasonable to attribute these long-wavelength absorption peaks to direct ground-state dimer absorption.

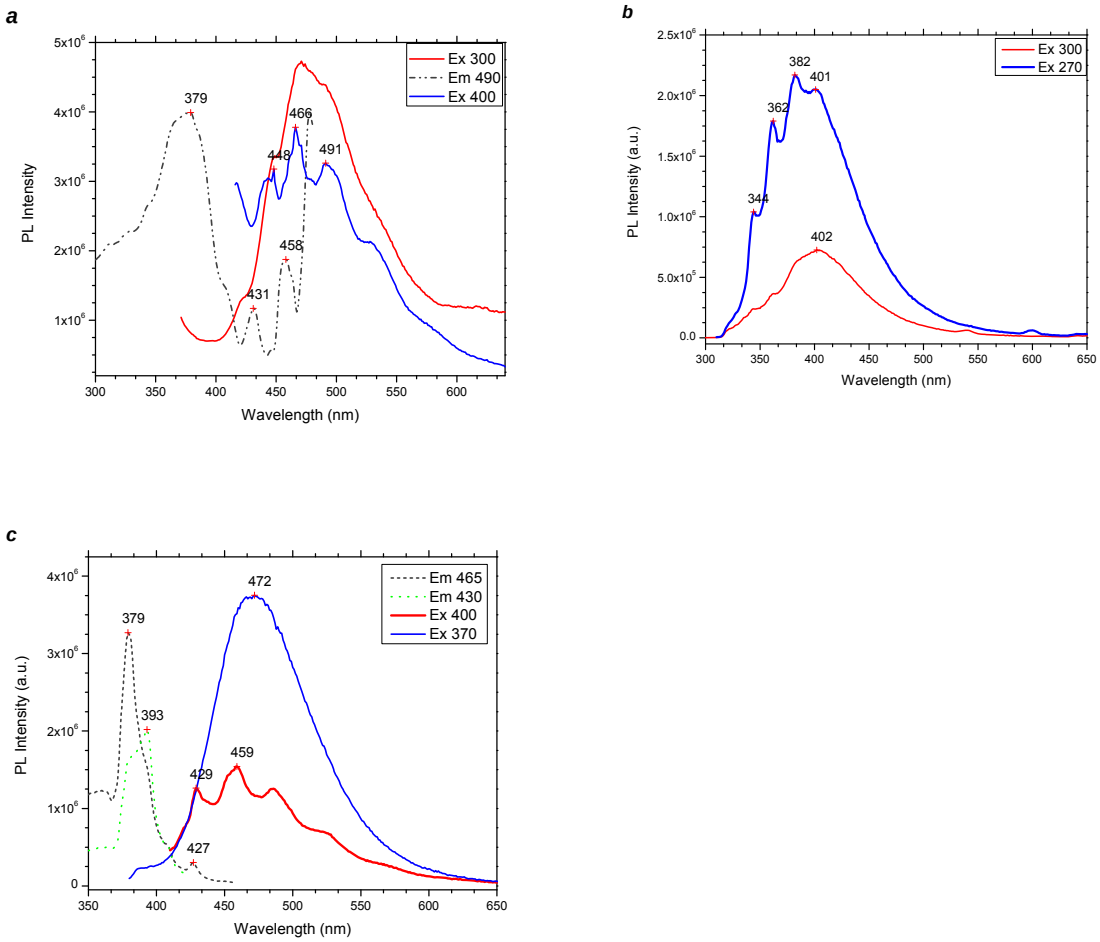


Figure 2.4. Emission spectra of pyrene crystals (a), solution of 0.1M DNP in cyclohexane (b), and solution of 0.1M pyrene in cyclohexane (c), at ambient temperature, upon selective excitation.

Pyrene crystals, when selectively excited at 400nm, also produce a structured emission (Figure 2.4a), which spans the same wavelength range as the broad emission previously reported by Birks.[9]

The unstructured profile for the pyrene excimer band has been attributed to dissociation before completion of a vibronic cycle,[3] while the contrasting situation upon direct dimer absorption may explain the presence of vibronic structure in our spectroscopic data (Figure 2.4a). This result is still surprising given that (a) the vibrational energy associated with the intermolecular motion is expected to be at a low frequency in the region of typical phonons (< 100 cm^{-1}), and (b) the ground-state is expected to be rather repulsive at the geometry of the excimer fluorescent state. However, this analysis addresses only the major distortion related to the intermolecular bonding while the experimentally found vibronic spacing of ~ 1360 cm^{-1} must correspond to other vibrational modes along the multidimensional distortion coordinate. Further electronic and vibrational studies are clearly warranted.

DNP (Figure 2.1), which exhibits intramolecular excimer formation in concentrated solutions,[5,10] was also tested to replicate these anomalous photophysical features exhibited by pyrene. The absorption spectra of a 0.1M solution of DNP was obtained and this revealed absorption bands at 300nm and 318nm, which had previously not been reported (Figure 2.2b). As shown in Figure 2.4b, selective excitation of the concentrated DNP solution, using these long-wavelength bands, resulted in a structured profile, which was super-

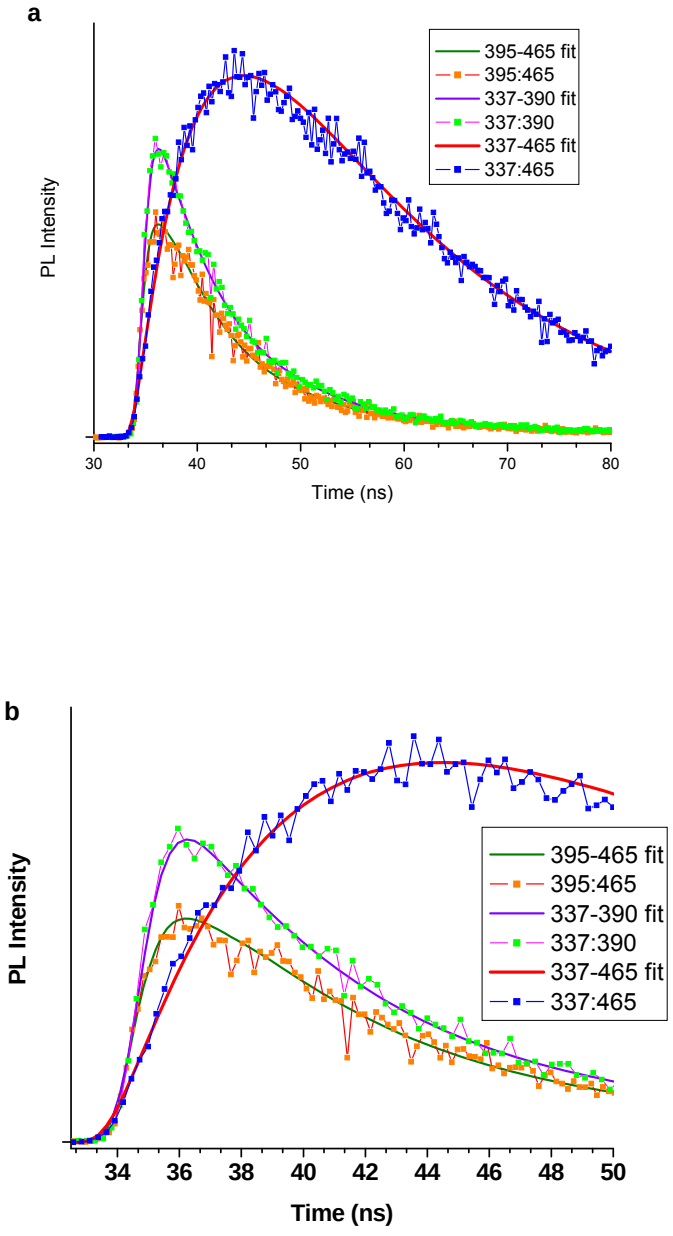


Figure 2.5 A qualitative comparison ot (a) lifetimes (b) risetimes in pyrene monomer, dynamic excimer, and pre-associated excimer of 0.1M pyrene in cyclohexane.

Table 2.1. The Time Dependent Data Of Pyrene Emission In Cyclohexane

	0.1M		0.02M	
	Rise-time / ns	Decay time / ns	Rise-time / ns	Decay time / ns
Dynamic Excimer ($\lambda_{Ex.}$ 337 nm)	1.467	12.47	6.17	11.3
Ground-state Excimer ($\lambda_{Ex.}$ 395 nm)	0.3942	8.285	0.1138	5.9

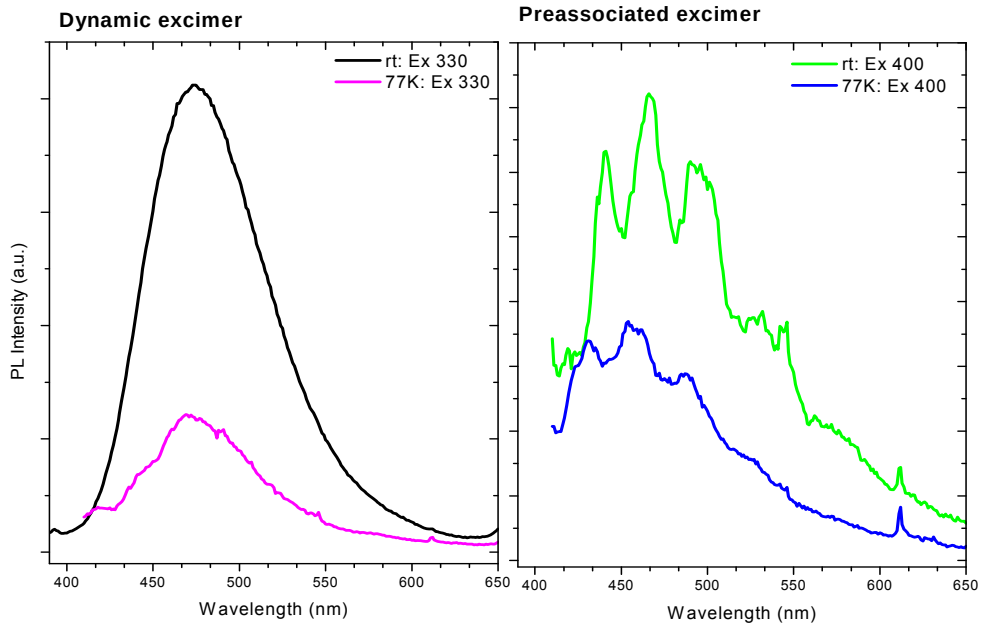


Figure 2.6 Side by side comparison of dynamic excimer formation and pre-associated excimer formation of 0.1M pyrene in cyclohexane at (a) ambient temperature (b) 77K.

imposable on the broad excimer emission obtained by exciting at monomer wavelengths. A value of 1363 cm^{-1} was also obtained for the vibronic spacing of the structured DNP excimer, which is identical to that obtained for pyrene.

Further distinctions of the new structured excimer fluorescence from the conventional unstructured band are obtained by both time-resolved and temperature-dependent luminescence measurements using selective dimer versus monomer excitation. Table 1 shows the time-resolved data. The excimer emissions were monitored at the same wavelength (465 nm) in the same solution sample. Here, the results show that dimer excitation (λ_{ex} = 400 nm) leads to a rise time that is significantly shorter than that obtained with selective monomer excitation (λ_{ex} = 337 nm). Since the conventional route for excimer formation involves diffusion and subsequent collision of an excited monomer with a ground-state monomer, a significant rise time is usually obtained and is reproduced in Figure 3. But with selective ground-state dimer excitation in solution, no long diffusion times are needed, similar to the situation in the solid state wherein molecules are packed in pairs giving rise to short rise times in the ps regime. A qualitative illustration of the preceding concept is seen in Figures 2. 5a and 2.5b which portray the different lifetimes (Figure 2.5a) and the different rise-times (Figure 2.5b), obtained for pyrene monomers, dynamic excimers and static excimers. Temperature dependent studies of pyrene in solution show that the structured excimer emission becomes stronger upon cooling to 77 K. This is in sharp contrast to the temperature dependent behavior for the unstructured pyrene excimer emission wherein cooling inhibits diffusion. This contrast, using the same solution sample, was established (Figure 2.6) upon selective excitation and reproduced for several concentrations.

2.4. Conclusion

Bonding between pyrene molecules is usually assumed to be nonexistent in the electronic ground-state. However, it has become evident that this is an oversimplification based on numerous studies in the latter part of the twentieth century. Nevertheless, the experimental evidence to date, with the exception of data published by Khakhel,[4] has been indirect - typically in the form of slight red shifts in the monomer absorption or excitation bands in samples exhibiting so-called “static excimer” emissions. Here direct spectroscopic evidence with distinct bands due to dimer formation taking place in both concentrated pyrene solutions, pyrene crystals and concentrated solutions of DNP is shown. The situation here is not different from that in the Hg_2 vapor[11] or in solutions and solids of dicyano Au(I) and Ag(I) complexes, which have been reported to exhibit excimer emissions upon exciting with oligomer bands that result from the weak ground-state metallophilic interactions.[12]

In the foremost review on preassociated pyrenes,[3] it was concluded that: “The selection of the excitation wavelength merits consideration. If it were possible to excite preassociated pyrenes to the exclusion of isolated pyrenes (or vice versa), the profile of the excimer emission would vary with excitation wavelength.” I have shown here that this scenario is possible, leading to distinctions of preassociated *vs*. predissociated pyrene excimer fluorescence bands not only in the emission profile (structured *vs*. unstructured), but also in excitation, time, and temperature profiles. The work is continuing to further

characterize the ground- and excited-state association of pyrene and other PAHs that are known to form excimers.

CHAPTER 3

PHOTOLUMINESCENCE OF 2,7 DIAZAPYRENE

3.1 Introduction

Though not as extensively studied as pyrene, a literature search for diazapyrene is bound to produce some studies of the photoluminescence properties of this compound. Notable among these studies include the work of Sotiriou-Leventis et al, which describe the packing structures for 2,7-diazapyrene salts[13] for which the absorption and emission profiles they obtained at standard conditions is nearly identical to what I obtained for diazapyrene solutions.

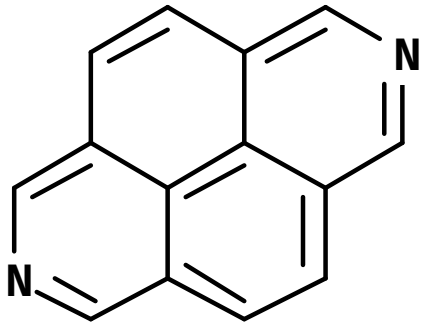


Figure 3.1. Structure of 2,7-diazapyrene.

In addition, Cejas and Raymo[14] studied films of diazapyrene derivatives, and various concentrations of diazapyrene in MeCN. They obtained absorption spectra at 320nm and 340nm respectively. They also obtained long wavelength

peaks at around 390nm and 410nm respectively. These values were taken at a concentration of 10^{-5} M in MeCN and at standard conditions. Fluorescence spectra, which were obtained at 10^{-7}M concentration in MeCN and also at standard conditions revealed excitation peaks at around 320nm and 345nm respectively and emission peaks at 420nm and 450nm respectively. My work below builds on the already published[14] photoluminescence properties of diazapyrene.

3.2. Experimental Section

The compound 2,7-diazpyrene has been provided to us from our collaborators at UT-Dallas. The compound has been as used as received without further purification. The photophysical measurements have described earlier in Chapter 2.

3.3. Results and Discussion

As shown in Figure 3.2a, I was able to reproduce some of the short wavelength peaks reported by Cejas and Raymo,[14] however, no peaks were obtained at 400nm, and 430nm except for a weak inflexion point at 432nm, (Figure 3.2b), when a high concentration was used (i.e. 10^{-2}M diazapyrene in butyronitrile)

I also obtained similar profiles in excitation and emission within the same ranges (Figure 3.3), when an excitation wavelength 330nm was used. In addition to the peaks obtained by Cejas and Rojas, however, a structured long-wavelength emission profile was obtained, with peaks at 473nm and 503nm. This profile is

notably similar to the structured dimer emission profile obtained for pyrene at high concentrations. Unlike in pyrene, however, the emission profile was obtained at standard conditions and disappeared when the solution was cooled to 77K.

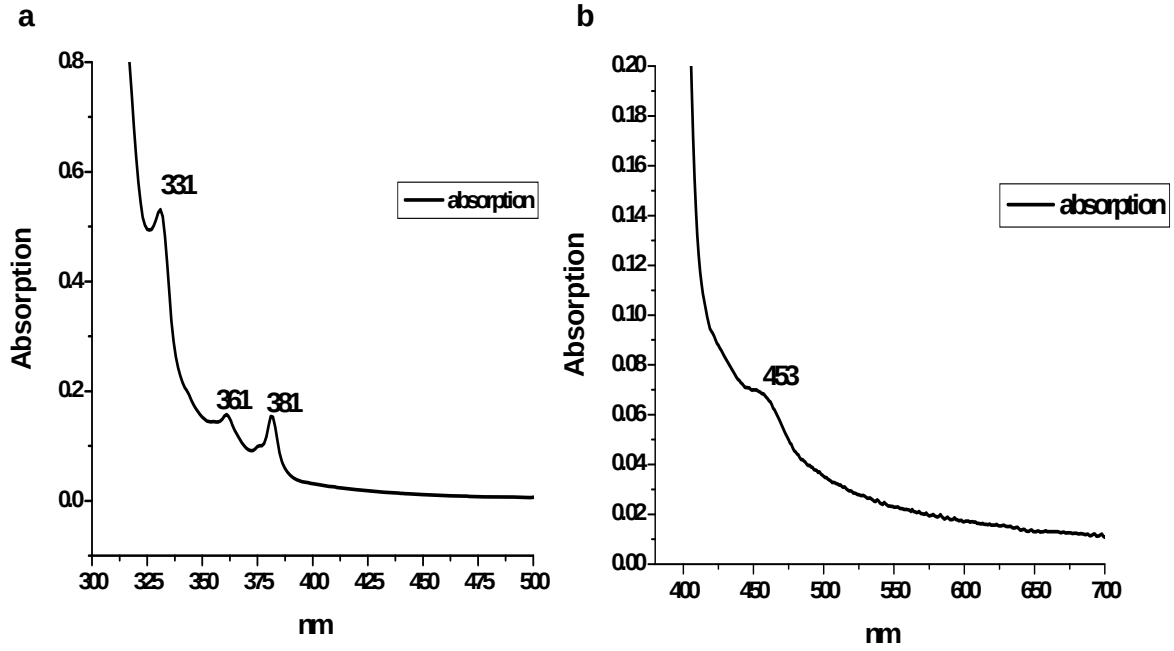


Figure 3.2 Absorption spectra of diazapyrene solutions: $1x10^{-5}$M diazapyrene in butyronitrile (a), and $1x10^{-2}$M diazapyrene in butyronitrile (b), at ambient temperature and at a path length of 1cm.

Time resolved studies of this long-wavelength emission correspond to dimerization on a timescale as occurs in static dimer formation, and is markedly similar to that obtained for the diazapyrene monomer (Figure 3.3). The lifetime measured for the diazapyrene monomer at 337nm excitation was 2.3 ns and that measured for the dimer at 430nm was 2.49 ns. This profile is, however, not enhanced by depressed temperatures, but disappears. This is unexpected.

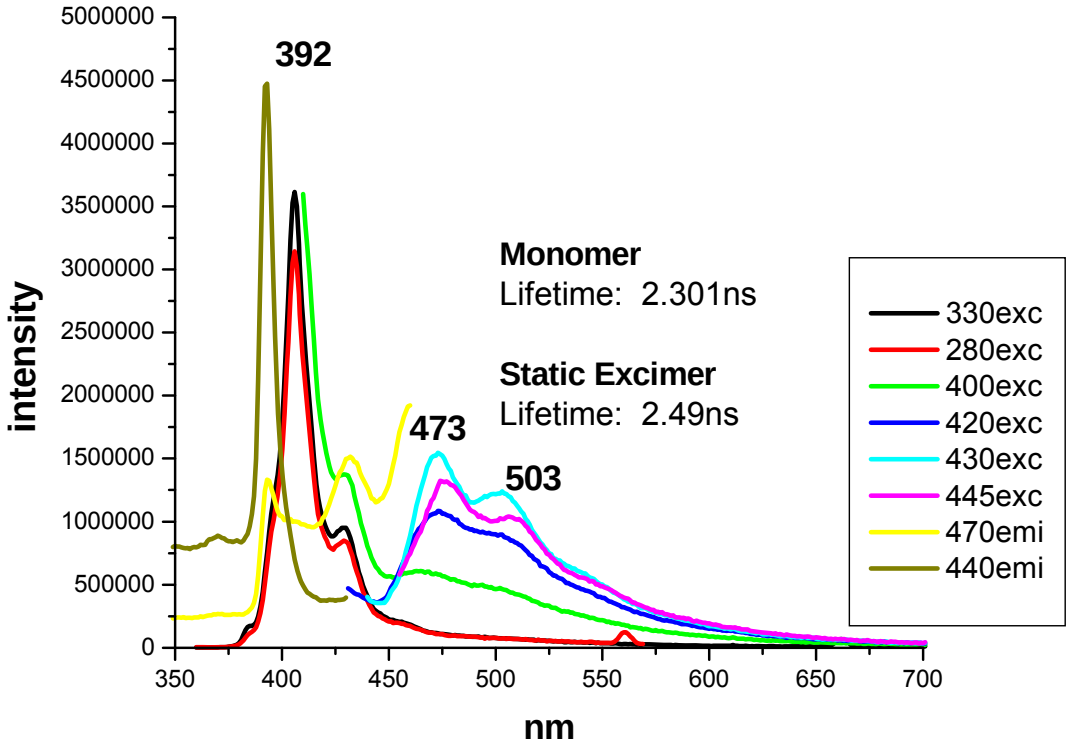


Figure 3.3 Excitation and emission spectra of 1x10-^{2}M diazapyrene at ambient temperature, showing varied emission profile with varied excitation wavelengths.

In addition to formation of static excimers, three additional properties of diazapyrene solutions, yet to be reported in current literature, were discovered in our studies:

1) Exhibition of delayed fluorescence
2) Formation of a long-wavelength unstructured excimer profile at 77K
3) Charge transfer from pyrene to diazapyrene

3.3.1. Formation of a Long-Wavelength Unstructured Profile At 77K

As discussed earlier with pyrene, dynamic excimer formation, characterized by a broad, unstructured profile is almost exclusively obtained at high temperatures. When diazapyrene in butyronitrile is cooled, however, a broad, structure-less emission profile is obtained at long-wavelengths (Figures 3.4, 3.5 and 3.6). This profile, only occurred in highly concentrated solutions of diazapyrene, and was generally not reproducible in other solvents besides butyronitrile. In THF, however, the profile was weakly detected as shown in Figure 3.6.

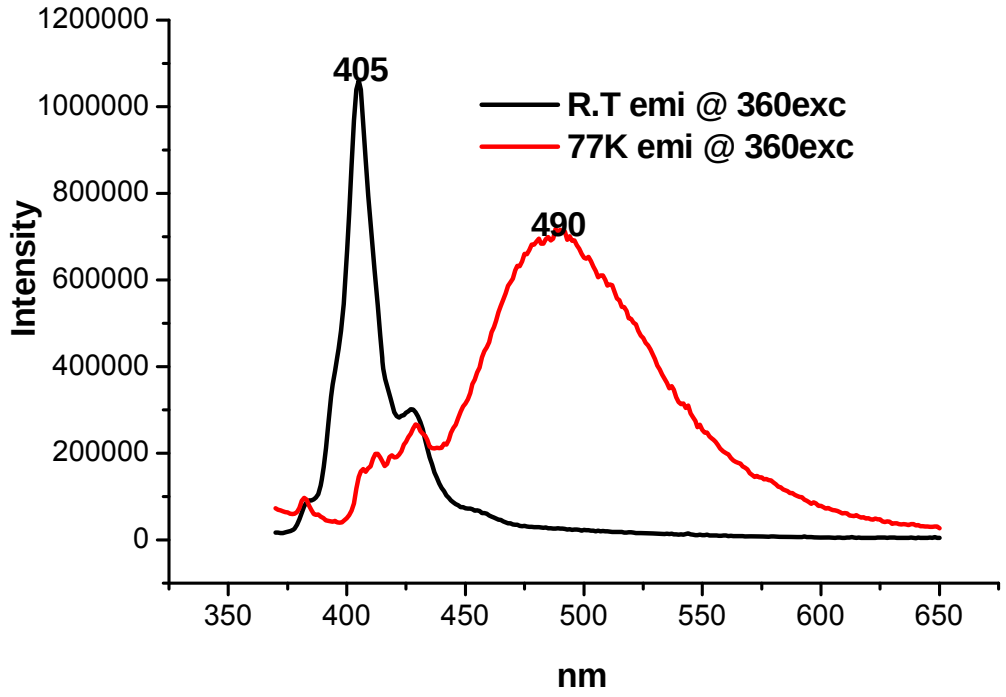


Figure 3.4 comparison of the emission profiles of 10^{-2}M diazapyrene in butyronitrile at ambient temperature and at 77K, with an excitation wavelength of 360nm.

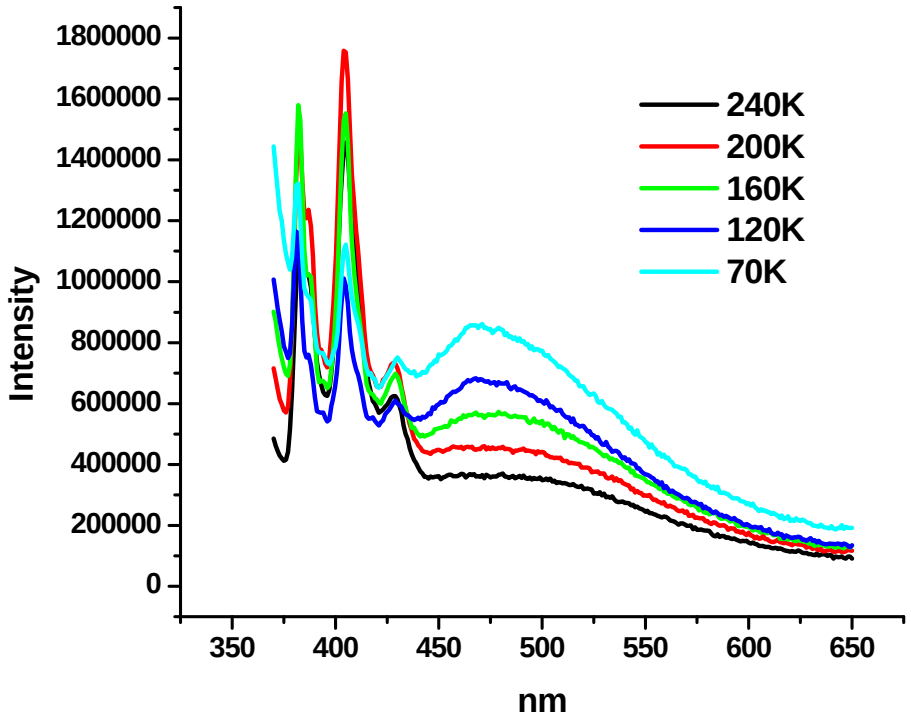


Figure 3.5 Emission profiles of 10^{-2}M diazapyrene in butyronitrile at various temperatures.

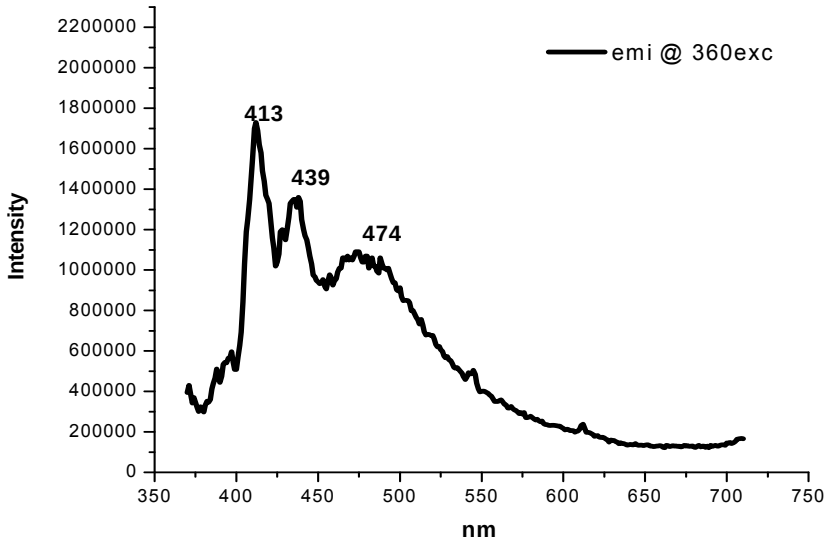


Figure 3.6 Emission profile of diazapyrene in THF at 77 K.

3.3.2. Delayed Fluorescence

As discussed in the introduction of this document, a delayed fluorescence may occur when an electron in a singlet excited state, undergoes intersystem crossing, and then reverts back to the singlet state before undergoing fluorescent decay. Repopulation of the singlet state is caused by quenching of the triplet state.[15] Quenching of the triplet state may occur through triplet-triplet annihilation or by singlet oxygen species. A solution of diazapyrene in 2:1 ether: ethanol produced a fluorescent spectrum, similar to what I obtained for diazapyrene solutions. However, the lifetime measured for diazapyrene in ether/ethanol solution was a remarkably long lifetime of 4.33 seconds (Figure 3.7). This phenomenon can only be explained by the theory of delayed fluorescence. This may have occurred in the ether/ethanol solution, as opposed to any of the solvents used, because the ether/ethanol mixture has a much lower viscosity and the rate of triplet-triplet quenching increases with decreasing viscosity.[15] Also the quantum yield for the delayed fluorescence may be much higher in the mixture than in the other solvents used.

3.3.3. Charge Transfer from Pyrene to Diazapyrene

A 1:1 mixture of diazapyrene and pyrene, gave us result worth pursuing. In a 1:1 mixture of diazapyrene and pyrene, it was noticed that the excitation profile strongly resembled that of pyrene however the emission profile was similar to that of diazapyrene. This led us to believe that some form of charge

transfer, from excited pyrene molecules to diazapyrene molecules was responsible for this emission.

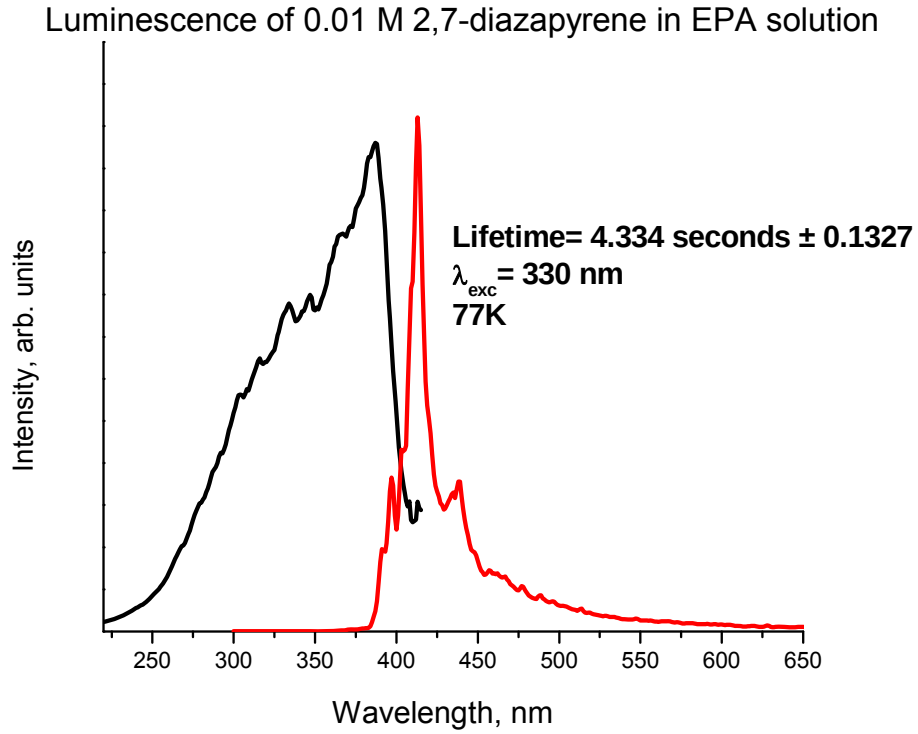


Figure 3.7 Delayed fluorescence emission of diazapyrene at 77K and at 330nm excitation.

To test this hypothesis, a time resolved study of the mixture was conducted using various delay times. As expected, the emission peak at 415nm, which was due to pyrene, quickly diminished with intensity while that of diazapyrene remained prominent or slightly increased in intensity, indicating a charge transfer from pyrene to diazapyrene.

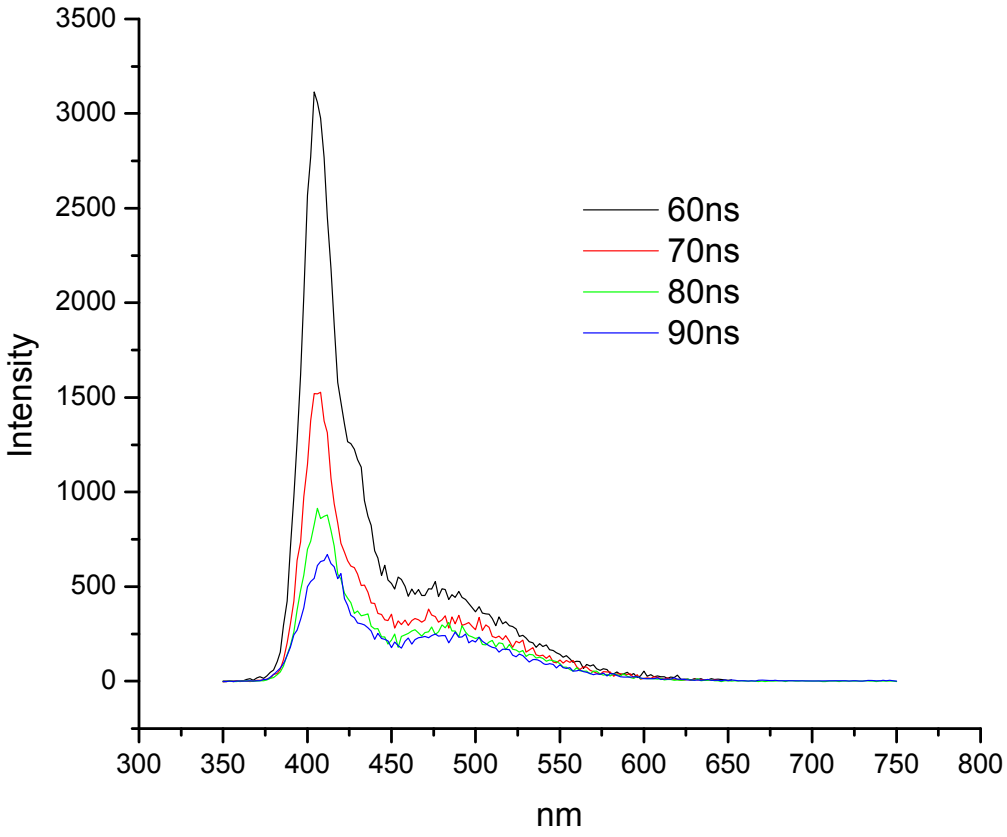


Figure 3.8.Time-resolved spectra of 1:1 diazapyrene: pyrene in butyronitrile at varied delay times.

In addition to time resolved studies rise-time/lifetime studies were also performed. The rise-time for diazapyrene, which represents the time taken for the formation of the diazapyrene emitting species, was very long at 6.51 ns, compared with that of pure diazapyrene. The rise-time I obtained when I excited at a wavelength of 337 nm proved conclusively that the emission profile obtained was due to diazapyrene emission subsequent to charge transfer from an excited pyrene species.

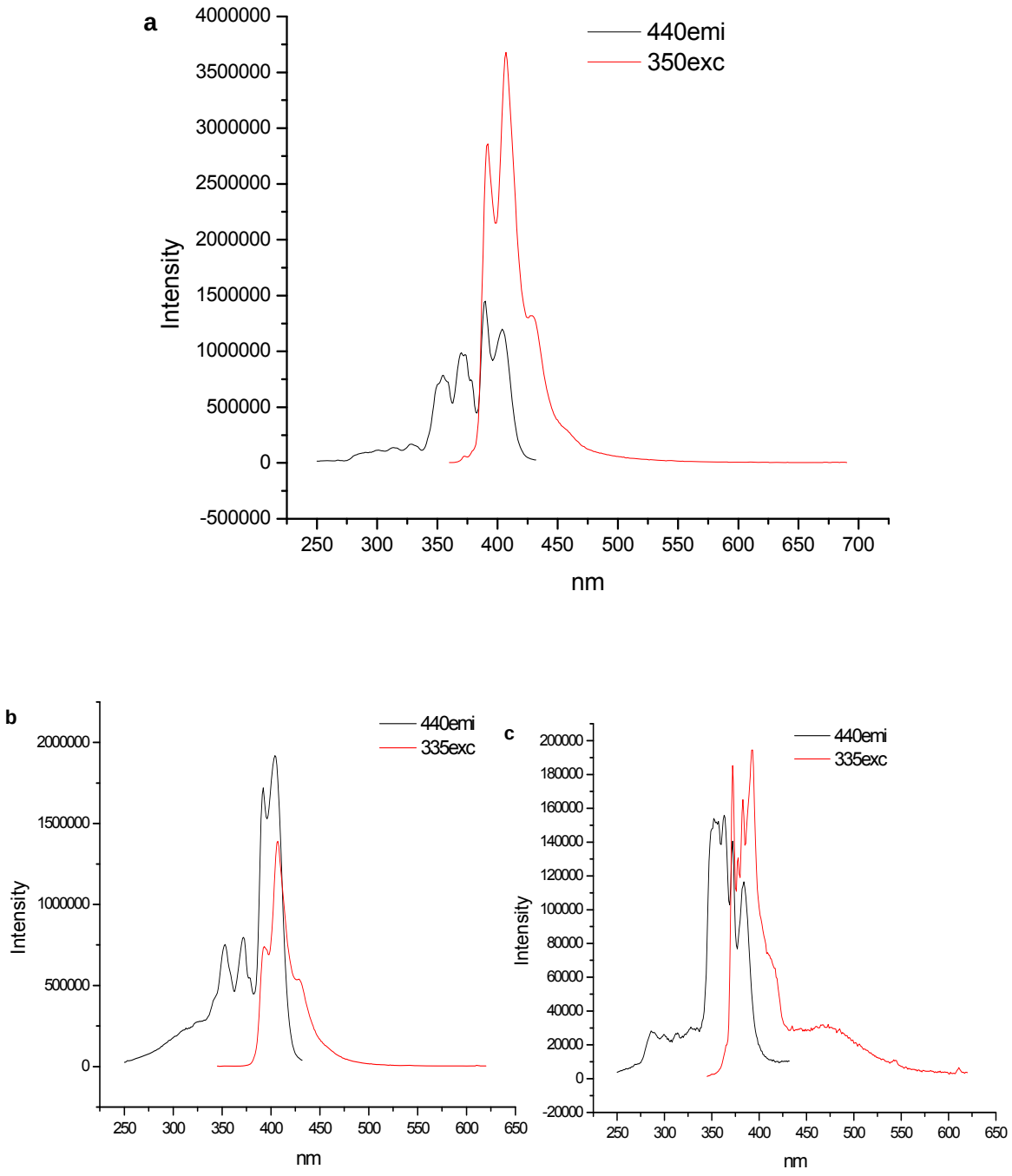


Figure 3.9 Luminescence spectra of (a) 1:1 Pyrene: diazapyrene in DCM, (b) 10^{-3}M diazapyrene in DCM, (c) 10^{-3}M pyrene in DCM

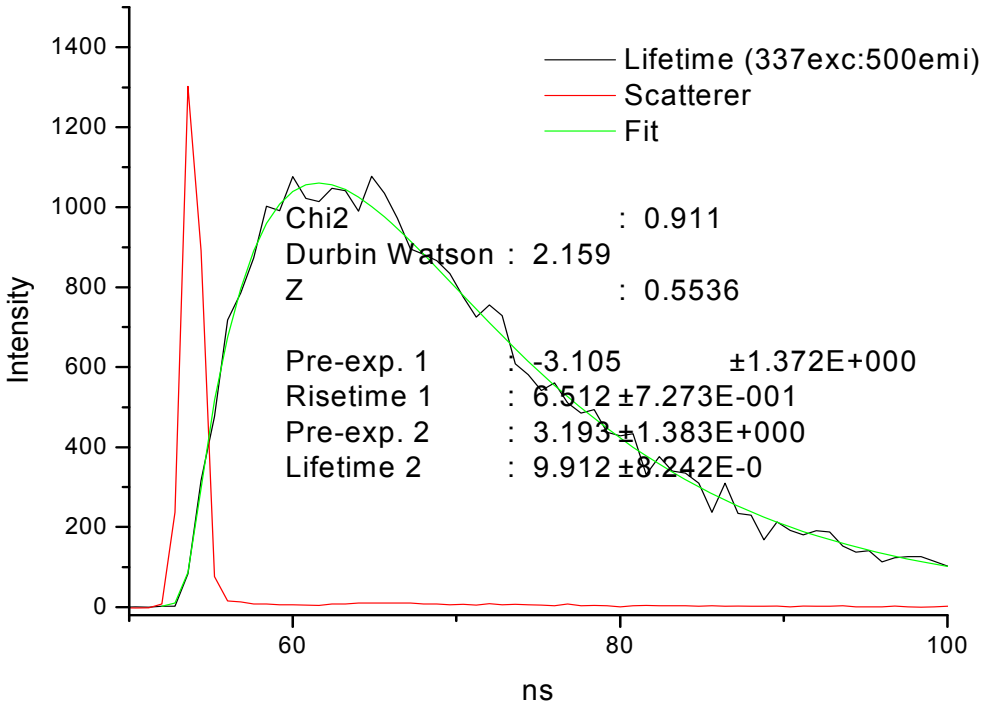


Figure 3.10. Risetime and lifetime of a 1:1 mixture of diazapyrene and pyrene at ambient temperature in butyronitrile

3.3.4. Conclusion

Diazapyrene is a strongly luminescent molecule, with interesting luminescent properties which have only been marginally investigated. My work on diazapyrene shows that the compound illustrates some significant principles of luminescence such as delayed fluorescence, charge transfer, dynamic and static excimer formation, which are not easily found in a single compound. My work also raises some important questions about the atypical behavior of the unstructured, and the structured profiles of the diazapyrene excimeric emission.

Answering these questions may help to further understand the behavior of static versus dynamic excimers.

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